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(54) **Monoacrylate ester coating compositions**

(57) A curable coating composition contains at least an acrylate ester composition. Preferably the coating composition is a UV curable coating composition and/or an anaerobically curable coating composition suitable for preparing a UV curable anaerobic adhesive or sealant or the like.

GB 2 283 975 A

COATING COMPOSITION

The present invention relates to a coating composition. In particular the present invention relates to a curable coating composition suitable for use as an adhesive, sealant, encapsulant, protective coating, mastic or the like.

Further in particular, the present invention relates to a UV curable coating composition and/or an anaerobic curable coating composition - such as a UV curable anaerobic adhesive or sealant or the like.

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More in particular, the present invention relates to a method of rapidly bonding substrates, such as metal to other parts, to provide a leak-proof join using a UV-curable anaerobic sealant composition, in addition to the compositions *per se*. More particularly, the present invention relates to a method of rapidly bonding a metal conduit to a metal panel to provide a leak-proof join, and especially an aluminium conduit to an aluminium panel, such as a car radiator or other similar heat exchange panel.

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In some areas of industry, substrates are coated (all or in part) with a coating composition. The nature of the coating composition will naturally depend on its purpose. For example, with coating compositions for use as adhesives it is sometimes desirable or even necessary that the coating composition can fairly quickly form a strong bond between two substrates - such as two metal substrates which need not be of the same metal, a metal substrate and a non-metal substrate (such as glass), or two non-metal substrates which need not be of the same material (such as glass and rubber). If the coating composition is for use as a sealant, likewise it is sometimes desirable or even necessary that the coating can fairly quickly form a good seal. The same is true for coating compositions for use as intermediate coatings - i.e. to separate one substrate from another.

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With particular reference to coating compositions for use as adhesives, it is known that the formation of a leak-proof join between a metal conduit and a sheet metal panel, such as are frequently required in the construction of metal (such as aluminium) heat exchange or car radiator panels, can present many problems. This is particularly exemplified in a mass production line, where the rapid formation of a completely water-tight bond between the conduit and the panel is vital. In a typical method of forming such a join, one end of the conduit is inserted as a close fit in a corresponding hole in the panel and either welded therein or bonded therein, e.g. by means of an anaerobic adhesive or sealant which forms an extended bead of sealant along the line of the join as well as between the mating surfaces. Whilst that type of join has the capacity to provide a strong leak-proof bond between the panel and the conduit, the exposed bead of anaerobic sealant around the join is relatively slow curing, so that the formation of such a join is time consuming, and not suitable for a mass production line.

In JP-A-57119970 Matsushita Electrical Industries KK have disclosed a method of securing a rotor to a shaft, which comprises applying a UV-curable anaerobic composition between the rotor and the shaft, curing the external bead of anaerobic compositions by exposure to UV-light to form a fillet, whilst allowing the composition remaining between the two parts to cure anaerobically at room temperature or with heating. Preferred for this purpose are anaerobically curable methacrylic monomers (called "acrylate" resins). A preferred composition consists of 20-70 p.b.w. of a hydroxyalkyl methacrylate and 30-70 p.b.w. of an adduct of bisphenol-A and methacrylic acid, from 0.1 to 10 p.b.w. of a photosensitiser and optionally other minor components such as polymerisation accelerators, inhibitors, colouring agents, tackifiers etc. Such compositions are said to have excellent adhesive and UV-curing properties. Suitable photosensitisers included benzoin, acetophenone and anthraquinone.

There are however problems associated with the compositions of JP-A-57119970. In this regard, they are essentially rigid curing compositions which form a mechanical key between the rotor and the shaft, rather than a truly adhesive bond.

Those rigid-curing UV-curable anaerobics are therefore of little value when it comes to situations where a truly adhesive bond is required, that is to say, a bond of high peel, cleavage and sheer strength.

- 5 A need therefore exists for a coating composition that can give the desired characteristics in a short period of time.

In particular, there is a need for such a coating composition but wherein the coating composition is a UV-curable coating composition and/or an anaerobically curable
10 coating composition.

More in particular, there is a need for a UV-curable anaerobic adhesive composition providing high peel, cleavage and sheer strengths, especially on light weight metals and metal alloys, and in particular on non-rigid substrates such as thin sheet
15 aluminium.

According to a first aspect of the present invention there is provided a curable coating composition comprising a curable monomer and at least one polymerisation initiator; wherein the curable monomer is a monoacrylate ester of the formula (I)
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where R is an alkyl or cycloalkyl group of up to 20 carbon atoms, or an alkyl or cycloalkyl group of up to 20 carbon atoms the carbon atom chain of which is interrupted by one or more ether oxygen atoms (-O-).
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According to a second aspect of the present invention there is provided a method of coating (all or partially) a first substrate, comprising coating the first substrate with a composition according to the present invention, and exposing (all or part of) the coating to conditions to initiate polymerisation of the composition.
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According to a third aspect of the present invention there is provided a solid coating comprising a cured coating composition according to the present invention.

According to a fourth aspect of the present invention there is provided the use of a monoacrylate ester of the formula (I) as a curable component of a coating composition.

- 5 Optionally, R of formula (I) can be an alkyl or cycloalkyl group of up to 20 carbon atoms containing one or more substituents selected from -OH, -CN, aryloxy (e.g. phenoxy), and -NH₂.

- 10 Preferably the at least one polymerisation initiator is at least selected from: a radiation polymerisation initiator, an anaerobic polymerisation initiator and a thermal polymerisation initiator.

- 15 Preferably the at least one polymerisation initiator is at least a radiation polymerisation initiator and/or an anaerobic polymerisation initiator.

- 20 Preferably the at least one polymerisation initiator is at least a radiation polymerisation initiator, preferably a photosensitive polymerisation initiator.

- 25 Preferably the at least one polymerisation initiator is a UV polymerisation initiator.

- 30 Therefore, according to a first preferred aspect of the present invention there is provided a UV curable coating composition comprising a UV curable monomer and a photosensitive polymerisation initiator; wherein the UV curable monomer is a monoacrylate ester of the formula (I).

- 35 According to a second preferred aspect of the present invention there is provided an anaerobic curable coating composition comprising an anaerobically curable monomer and an anaerobic polymerisation initiator; wherein the anaerobically curable monomer is a monoacrylate ester of the formula (I).

According to a third preferred aspect of the present invention there is provided a UV-curable anaerobic adhesive coating composition comprising i) a monoacrylate ester of the formula (I); ii) an anaerobic polymerisation initiator (preferably an anaerobic redox polymerisation initiator); and iii) a photosensitive initiator.

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According to a fourth preferred aspect of the present invention there is provided a method of coating (all or partially) a first substrate, comprising coating the first substrate with a composition according to the first preferred aspect of the present invention, and exposing (all or part of) the coating to UV radiation.

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According to a fifth preferred aspect of the present invention there is provided a method of coating (all or partially) a first substrate, comprising coating the first substrate with a composition according to the second preferred aspect of the present invention, and subjecting (all or part of) the coating to anaerobic conditions.

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According to a sixth preferred aspect of the present invention there is provided a method of forming an adhesive bond between a first substrate and a second substrate, which comprises applying between the substrates a UV-curable anaerobic adhesive coating composition according to the third preferred aspect of the present invention, and exposing at least some of the applied adhesive coating to UV-radiation, thereby to initiate the photochemical cure of the adhesive, at least in the areas thereof that are exposed to the radiation, whilst allowing the remainder of the applied composition to cure anaerobically.

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25 Preferably the composition contains one or more other acrylate monomers selected from the corresponding esters of acrylic acid or methacrylic acid and the polyacrylic and methacrylic esters of acrylic or methacrylic acid and a polyfunctional alcohol or ether-alcohol.

30 Preferably the monoacrylate ester is t.butylcyclohexyl acrylate.

Preferably the composition contains a free radical initiator.

Preferably the composition contains up to about 60% (preferably up to about 50%) by weight, based on the total composition, of a low molecular weight elastomeric polymer having a number average molecular weight in the range 1,000 to 6,000 and having one or more reactive groups in a pendant or terminal position on the elastomeric polymer molecule, the reactive groups being at least any one of: -
5 CH:CH₂, -COOH, -SO₂Cl, -SH, -NH₂ and -OC(O)C(R):CH₂ wherein R is H, C₁-C₄ alkyl or halogen.

Preferably the method comprises forming an adhesive join between a first substrate
10 and a second substrate, which comprises applying the adhesive coating composition between the mating surfaces of the two substrates and in a sufficient quantity to form an external bead of uncured adhesive along the line of the join, and exposing the external bead of uncured adhesive to UV-radiation thereby to initiate the photochemical cure of the bead, whilst allowing the adhesive between mating surfaces
15 to cure anaerobically.

Preferably the method is for the formation of an adhesive bond between the end of a tubular first member inserted as a close fit in a correspondingly sized hole in a second member, and wherein said external bead of uncured adhesive completely
20 encircles the said tubular member along the line of the join between it and the said second member, thereby to form a fully leak-proof adhesive join between the first and second members.

Preferably the method is for the formation of a leak-proof adhesive join between a
25 tubular inlet of or an outlet connector to a heat exchange panel as the first member and a heat exchange panel as the second member.

Preferably the heat exchange panel is a radiator for the cooling system of a motor vehicle.

30 Alternatively the coating composition may be applied to a substrate so that it flows into a channel or groove or joint whereupon it is then cured.

Preferably the first substrate is a metal substrate.

Preferably the first substrate is an aluminium substrate.

- 5 Alternatively the method may be for the formation of an adhesive bond between two substrates, one of which at least is of glass, or other material transparent to UV-light, and wherein the photochemical cure of the applied adhesive is initiated by exposing the applied adhesive to UV-radiation through the UV-transparent substrate. Preferably the method is for the formation of a glass-to-glass bond, a glass-to-metal
10 bond or a glass-to-ceramic bond.

The polymerisable monomer of the coating composition of the present invention is at least an acrylate monomer, as opposed to a methacrylate monomer of the prior art, especially those disclosed in JP-A-57119970.

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- The results achieved by the compositions of the present invention are particularly surprising. The key advantage of the present invention is that it provides a coating composition that can be cured to provide an excellent coating by exposing the composition to conditions to initiate polymerisation of the composition - such as by
20 exposure to UV-radiation and/or under anaerobic conditions. More in particular, the present invention allows for the provision of a coating composition having dual curability - namely a UV curable and an anaerobically curable coating composition.

- Other advantages of the present invention are that it provides an adhesive having high
25 peel, cleavage and sheer strengths, especially on light weight metals and metal alloys, and in particular on non-rigid substrates such as thin sheet aluminium.

- Another important advantage is that the cured coating compositions are clear. This means that the coating compositions can form an almost invisible join between two
30 substrates. This is particularly advantageous in the construction of double glazing when the coating composition is used to bond the edges of a folded strip of, for example, aluminium.

The present invention also provides an excellent sealant or protective covering which may, for example, be used to cover a hinge or a catch connection to protect it from rusting etc. This is particularly advantageous in the automotive industry for coating the bolts connecting a catch or latch to a car bonnet.

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The present invention also provides an excellent bonding and/or sealing intermediate layer. This is particularly advantageous in the manufacture of bullets and the like. In particular, the coating composition is especially suited for the preparation of firing pins for use with safety belts in the automotive industry. In this regard, the coating composition forms an intermediate layer between the firing pin and its housing such that the pin can move easily out of the housing upon triggering thereof by, for example, quick braking of the automobile.

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Other advantages will become apparent in the following description and examples.

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The term "coating composition" with regard to the present invention means any suitable coating composition for covering (all or part of) one or more substrates. The coating composition can be in liquid or in solid form, or intermediate forms thereof, or combinations thereof. The coating composition can serve two or more purposes. For example, the coating composition can at least be used for any one of an adhesive, a sealant and a protective intermediate layer. The coating composition can even be used in or as a caulk or a mastic. The coating composition can even be used for encapsulating articles - such as electrical or mechanical articles. The articles can be delicate articles such as items of jewellery.

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The term "curable" with regard to the monomers of the present invention means that the monomers can form polymers under the appropriate curing conditions, depending upon the choice of polymerisation initiator or initiators in the coating composition - such as exposure to radiation (preferably UV light), exposure to heat or exposure to anaerobic conditions.

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The term "radiation" in relation to the polymerisation initiator covers any suitable polymerisation initiator that is activated by a suitable spectral radiation. In particular, it includes photosensitive polymerisation initiators. More preferably it means a UV polymerisation initiator.

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The term "anaerobic" in relation to the polymerisation initiator covers any suitable polymerisation initiator that is activated by the substantial absence of oxygen.

10 The term "thermal" in relation to the polymerisation initiator covers any suitable polymerisation initiator that is activated by the application or exposure to heat - which can come from or be generated by any suitable source.

Thus, according to one highly preferred embodiment of the present invention there is provided an extremely high strength UV-curable anaerobic adhesive composition.

15 The UV-curable anaerobic compositions of the present invention are quite remarkable in retaining their stability in the presence of air or oxygen, yet cure extremely rapidly (1-2 seconds) when exposed to UV-radiation, as well as retaining their ability to cure anaerobically upon exclusion from air or oxygen, but without losing their cure speed.

20 The coating compositions of the present invention preferably contain a low molecular weight reactive rubber. Examples of suitable low molecular weight rubber are disclosed in GB-A-1505348 and GB-A-1550778. This rubber can, for example, provide a multi-cure adhesive composition having the rapid cure characteristics of a UV-curable resin on the one hand, whilst still retaining the characteristics of an
25 anaerobic adhesive on the other, and providing an extremely tough, flexible adhesive composition when cured, and capable of providing high strength flexible bonds between substrates of all kinds, e.g. metal-to-metal bonds, glass-to-metal bonds, glass-to-glass bonds, plastics-to-plastics bonds, plastics-to-metal bonds and plastics-to-glass bonds. Such compositions are therefore useful as highly versatile rapid cure
30 adhesives.

One highly preferred embodiment of the present invention is a UV-curable anaerobic adhesive comprising (preferably consisting essentially of):

i) an anaerobically polymerisable monomer system containing as its major monomeric component one or more monoacrylate esters of the formula



where R is an alkyl or cycloalkyl group of up to 20 carbon atoms, optionally containing one or more substituents selected from -OH, -CN, aryloxy e.g. phenoxy, and -NH₂, or an alkyl or cycloalkyl group of up to 20 carbon atoms, the carbon atom chain of which is interrupted by one or more ether oxygen atoms (-O-); and,

10 as an optional minor component, one or more other acrylate monomers as defined above; selected from the corresponding esters of acrylic or methacrylic acid, polyacrylic and polymethacrylic esters of acrylic or methacrylic acid and a polyfunctional alcohol or ether-alcohol, and acrylic acid or methacrylic acid:

ii) an anaerobic redox polymerisation initiator system;

15 iii) a photosensitive initiator system; and

iv) from 0-60% (preferably up to about 50%) by weight, based on the total composition, of a low molecular weight elastomeric polymer having a number average molecular weight in the range 1,000 to 6,000 and having one or more reactive groups in a pendant or terminal position on the elastomeric polymer molecule, such reactive groups being selected from: -CH:CH₂, -COOH, -SO₂Cl, -SH, -NH₂ and groups of the formula -OC(O)C(R):CH₂ where R is H, C₁-C₄ alkyl or halogen.

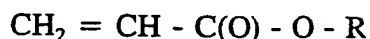
Another highly preferred embodiment of the present invention is a method of
25 adhesively bonding a first member to a second member to form a leak-proof adhesive bond therebetween, which comprises applying a UV-curable anaerobic adhesive as above defined both between the mating surfaces of the parts to be joined and as an external bead of adhesive along the lines of the join, exposing the external bead of uncured adhesive to UV-radiation to initiate curing of the external bead of adhesive
30 whilst allowing the anaerobic adhesive to cure anaerobically internally of the join and between said mating surfaces assisted, if desired, by the application of heat.

A further preferred embodiment of the present invention is a method of adhesively bonding a metal, e.g. aluminum, conduit to a metal panel, e.g. a car radiator or heat exchanger panel, to form an adhesive leak proof bond therebetween, which comprises inserting one end of the metal conduit as a close fit into a hole in the panel, applying
5 a UV-curable anaerobic adhesive, as above defined, to the join in a sufficient quantity to penetrate between the mating surfaces and to form a continuous external bead of uncured sealant around the line of the join, and exposing the external bead of uncured adhesive to UV-radiation to initiate the cure of the external bead whilst allowing the adhesive to cure anaerobically internally of the join between said mating surfaces.

10

Whilst the above preferred methods are particularly directed to the formation of a leak-proof adhesive bond between two members, and to this end uses a sufficient quantity of the anaerobic composition to form an external bead of uncured adhesive along the line of the join, which bead is then exposed to UV-radiation to initiate the
15 cure of the external bead whilst internally the cure is affected anaerobically, the anaerobic adhesives of this invention find utility in rapidly bonding other joins where a leak-proof bond is not of primary importance. They also have utility in a number of situations where a UV-curable adhesive is required. One such situation is in the formation of glass-to-glass bonds, glass-to-metal bonds, or glass-to-ceramic bonds,
20 such as are commonly used in the semiconductor and optical fibre industries, and where, following the application of the adhesive between two mating surfaces, curing of the applied adhesive layer is initiated photochemically by irradiation of the assembly with UV-light. Using that technique and the UV-curable anaerobic adhesives of this invention strong flexible glass-to-glass, glass-to-metal or glass-to-
25 ceramic bonds can be formed in as little as 1 to 2 seconds or less.

As indicated, the monomeric component of the compositions of the present invention is at least a monoacrylate ester of the formula:



30 where R is an alkyl or cycloalkyl group of up to 20 carbon atoms, optionally containing one or more substituents selected from -OH, -CN, aryloxy, e.g. phenoxy, -NH₂, and ether oxygen -O-, or a mixture of two or more thereof.

Suitable and preferred monoacrylate esters include, for example, methyl acrylate, ethyl acrylate, cyclohexyl acrylate, t-butyl cyclohexyl acrylate, 2-hydroxyethyl acrylate, 2-cyanoethyl acrylate, tetrahydrofurfuryl acrylate, 2-phenoxyethyl acrylate.

- 5 Usually two or more acrylate esters will be used, especially a mixture of a monoacrylate and a polyacrylate. Such mixtures will often also contain a small amount of acrylic or methacrylic acids as an additional monomer. The poly- and mono-acrylate can be typical acrylate esters used in anaerobic adhesives, which are useful also in the compositions of this invention. Examples of suitable monomers can
- 10 be found in the many previous patents and published patent applications relating to anaerobic adhesives and of which the following are representative: GB-A-1151916, GB-A-1347068, GB-A-1374351, GB-A-1505348, GB-A-1550748, GB-A-137535 and GB-A-1550778.
- 15 Suitable polyacrylate esters include, for example, ethylene glycol diacrylate, diethylene glycol diacrylate, neopentyl diacrylate and 1,1,1-trimethylol propane triacrylate.

- As already indicated, anaerobic adhesives based on acrylate esters generally contain
- 20 one or more catalysts, activators and inhibitors in admixture with the acrylate esters to provide the anaerobic curing properties. Likewise, the compositions of the present invention will also generally contain one or more such catalysts, activators and inhibitors.

- 25 The polymerisation initiators used in the compositions of the present invention may be suitable known initiators.

- For example, to provide the characteristic UV-curable characteristic aspect of the present invention, the coating compositions of the present invention will contain a
- 30 photoinitiator, usually in an amount of from 1-10% by wt. based on the total composition, more usually from 2-3%.

Preferably the photoinitiator is of the free radical type, for example, those sold under the trade name: IRGACURE, for example, either 2,2-dimethoxy-1,2-diphenylethane-1-one (Irgacure 651) or 1-hydroxycyclohexylphenylketone, or other similar compounds.

5

However, cationic photoinitiators, e.g. the triaryl sulphonium salts, are also effective.

The photoinitiator may be incorporated into the coating composition at any suitable stage, but is preferably added following blending of the monomers and the optional
10 reactive elastomer.

The catalysts that may be present in the compositions of the present invention can be any of the catalyst materials commonly used in the art. For example, tertiary amines and compounds containing a --CO--N< group may be used. Typical examples are
15 N,N-dimethyl-p-toluidine, tri-n-butylamine, 2,diethylaminoethanol, N-methylformamide, phthalimide, succinimide, o-benzoic sulphimide and dodecyl mercaptan. As activators there will generally be used a compound capable of forming free radicals, either directly or indirectly, such compounds typically including peroxy compounds, e.g. peroxides, hydroperoxides and peresters, such as cyclohexyl-
20 hydroxycyclohexyl peroxide, t-butyl hydroperoxide, t-butyl perbenzoate, hydrogen peroxide, cumene hydroperoxide, ethylene glycol dimethyl ether hydroperoxide and 2.5-dimethyl-2.5-di(t-butylperoxy)hexane.

The inhibitors that may be used in the coating compositions of the present invention
25 include naphthaquinone, hydroquinones, sterically hindered phenols and nitroxides.

Other additives, e.g. accelerators, viscosity modifiers, fillers, tackifiers, dyes and plasticizers may also be incorporated in the anaerobic curing composition as is conventional in the art.

30

The formulation and/or treatment of the coating composition to achieve the desired anaerobic curing properties will be according to principles and techniques established in the art such as, for example, by passage of air or oxygen through the mixture containing the monomeric ester or ester mixture, the catalyst, the activator and the inhibitor, until a stable composition capable of curing anaerobically is obtained.

The term "stable" here means a composition which when heated to either about 82°C or about 100°C will not gel in a period of 30 minutes or 300 seconds, respectively.

In some formulations, using certain combinations of catalyst and/or activator and/or inhibitor, the necessary stabilisation can be obtained without the necessity for oxygenation, as is known in the art. However, in the formulation of the preferred anaerobic curing compositions according to the present invention which contain a reactive elastomer, oxygenation with air or oxygen is the preferred stabilisation treatment.

The low molecular weight elastomers which are preferably incorporated into the multi-curing compositions of this invention to give improved shear strength, improved peel strength and improved impact resistance to the cured composition, are low molecular weight elastomers containing at least one reactive group attached to the polymer molecule, such reactive group being of the formula $-NH_2$, $-SH$, $-COOH$, $-SO_2Cl$, or $-OC(O)C(R):CH_2$, where R is as above defined, i.e. H, C_1 - C_4 alkyl or halogen, preferably hydrogen. The reactive elastomers used in accordance with this invention are rubbers which are soluble in the acrylate ester component of the anaerobic curing composition. Preferred are liquid elastomers having a number average molecular weight in the range 1000 to 6000, more preferably 2500 to 5000.

The preferred low molecular weight polymers have a backbone composed of polymerised butadiene units optionally with a proportion of polymerised acrylonitrile units.

Most preferred are butadiene and butadiene-acrylonitrile copolymer esters of acrylic acid or 2-alkyl substituted acrylic acids having a number average molecular weight between 3000 and 4000, and chlorosulphonated polyethylenes (HYPALON), including variants thereof.

5

Typical of such acrylate terminated butadiene and butadiene/ acrylonitrile copolymers are those sold by B.F. Goodrich Chemical Co. under their trade name Hycar, viz: Hycar VTB and VTBN which are vinyl terminated butadiene and butadiene/ acrylonitrile polymers, respectively, having number average molecular weights in the

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range 3000 to 6000.

Closely related to these are vinyl terminated butadiene/acrylonitrile copolymers containing pendant as well as terminal vinyl group and sold under the trade name Hycar VTBNX, which are particularly preferred.

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Other reactive liquid, elastomer-forming, low molecular weight polymers useful in this invention include:

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Hycar MTBN (mercapto terminated butadiene/acrylonitrile), molecular weight Mn 3270, acrylonitrile content 19.4%, and

Hycar ATBN (amino-terminated butadiene/acrylonitrile).

25

Besides the carboxy, amino, vinyl and mercapto terminated butadiene and butadiene/ acrylonitrile polymers listed above, other low molecular weight reactive elastomers suitable for use in the present invention include urethanised polybutadienes and halogenated polybutadienes, e.g. brominated polybutadiene, butadiene-styrene copolymers, polyisoprenes and polychloroisoprenes all containing a reactive group or groups as specified. Also suitable are low molecular weight chlorosulphonated polyolefins, e.g. chlorosulphonated polyethylene (HYPALON).

30

The low molecular weight reactive elastomers are preferably incorporated into the composition in amounts of up to about 60% (such as from about 1% to about 60%, preferably to about 50%) by weight of the total composition. They may be incorporated into the anaerobic curing composition at any suitable time during the mixing or stabilisation procedures. In the preferred technique, an anaerobic curing composition is first prepared by oxygenating a mixture of the acrylate ester containing the necessary activators, catalysts and inhibitors, adding the liquid reactive elastomer to the oxygenated mixture and continuing the oxygenation until the final mixture shows a gel time at 100°C of not less than 300 seconds.

10

To provide the characteristic multi-cure functionality of the highly preferred coating compositions of the present invention, a photoinitiator may be incorporated into an anaerobic composition of the present invention at any suitable stage. But preferably it is added to the stabilised anaerobic adhesive following blending of the monomers with the components of the initiator system and the reactive elastomer and subsequent oxygenation of the blend.

15

Typical and preferred UV curable anaerobic adhesives according to the invention are given in the following examples.

20

EXAMPLE I

Anaerobic formulation:

| | | <u>% by weight</u> |
|----|---|--------------------|
| 5 | t-butylcyclohexyl acrylate ¹ | 57.9 |
| | HYCAR VTBNX ² (1300 x 33) | 25.0 |
| | acrylic acid | 9.0 |
| | trifunctional oligoacrylate ³ | 2.0 |
| | saccharin | 1.0 |
| 10 | cumene hydroperoxide | 2.0 |
| | 1,4-naphthaquinone ⁴ | 0.2 |
| | tetrasodium EDTA ⁵ | 0.6 |
| | N,N-dimethyl-p-toluidine ⁶ | 0.3 |
| | 2,2-dimethoxy-1,2-diphenylethane-1-one ⁷ | 2.0 |

15

Footnotes:

- 1 IRR 164 (which is a trade mark) is supplied by UCB.
- 2 methacrylate functional butadiene-acrylonitrile oligomer supplied by B. F. Goodrich. (HYCAR VTBNX is a trade mark.)
- 20 3 EBCRYL 48 (which is a trade mark) is supplied by UCB.
- 4 as 5% solution in triethylene glycol dimethacrylate.
- 5 as 5% solution in 1:1 vol. water/isopropanol.
- 6 NL65/100 (which is a trade mark) is supplied by Akzo Chemie.
- 7 IRGACURE 651 (which is a trade mark) is supplied by Ciba-Geigy.

25

The monomeric components, including the low molecular weight elastomer HYCAR VTBNX, were blended with the components of the initiator system and oxygenated essentially in accordance with the general procedure set out in Example 1 of GB-A-1505348 to provide an initial toughened anaerobic formulation.

30

In more detail, the procedural steps were as follows:

1. t-butylcyclohexyl acrylate, acrylic acid, trifunctional oligoacrylate, 1,4-naphthaquinone and tetrasodium EDTA were blended in the amounts stated
5 above in a glass flask fitted with a non-metallic stirrer;
2. HYCAR VTBNX was then added in the amount stated above;
3. Saccharin was then added in the amount stated above and allowed to dissolve;
10
4. Cumene hydroperoxide was then added in the amount stated above;
5. The blended mixture was then aerated for about 15 minutes;
- 15 6. N,N-dimethyl-p-toluidine was then added in incremental amounts until the total amount added equalled the amount stated above;
7. The blended mixture was then tested for stability at 100°C for 300 seconds;
- 20 8. 2,2-dimethoxy-1,2-diphenylethane-1-one (i.e. the photoinitiator) was then added in the amount stated above; and
9. The blended mixture was then tested for stability at 100°C for 300 seconds.
- 25 The resulting composition was a liquid which, when confined in the form of a thin film between two substrates, cured rapidly to a solid polymer adhering the two substrates together.

Using the standard test of anaerobic stability at 82°C, the composition showed a gel
30 time in excess of 1 hr. The commercial standard for anaerobics requires a gel time under those conditions in excess of 30 minutes.

When tested on a degreased mild steel M8 nut and bolt, the composition gave a finger tight cure time of 10 minutes. After 1 hr. at 25°C the composition provided a torque strength of 1.3Nm rising to 2.6 Nm after 2 hours.

- 5 The ability of the composition alternatively to provide a rapid cure when exposed to UV radiation was tested under a Blue Point UV lamp (19.5 mW cm⁻², 365 nm) on various test samples providing a glass-to-glass bond, a glass-to-mild steel bond and a glass-to-aluminium bond. In each case, the handling time was 1 second or less, with the ultimate bond strengths being excellent in all cases.

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Flexibility of the cured composition following UV-cure was tested on a sample comprising a film of polyester bonded to abraded aluminium using the above composition and cured (1 sec) using the Blue Point UV lamp (19.5 mW cm⁻², 365 nm). The substrates were then subjected to a 180° bend without any loss of adhesion and without any cracking of the adhesive.

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The multi-cure composition thus shows a remarkable combination of properties: long-term stability - test compositions were still liquid after storage for 1-month under ambient (25°C) conditions - excellent bond strength when used as an anaerobic adhesive, with typical anaerobic cure times (finger tight cure 10 minutes), yet providing excellent properties as a UV-curing adhesive, with cure times as little as 1 second, and providing high strength, tough, flexible bonds between a variety of different substrates, e.g. glass-to-glass, glass-to-metal, metal-to-plastics or glass-to-plastics.

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Each of these results is surprising.

EXAMPLE II

Following the procedure outlined in Example I, an anaerobic adhesive was formulated containing

| | | |
|----|-------------------------------------|--------------------|
| 5 | | <u>% by weight</u> |
| | Hycar VTBNX (1300 x 33) | 24.27 |
| | t-butyl cyclohexyl acrylate | 38.91 |
| | Isobornyl acrylate | 9.70 |
| | Acticryl CL1039 ¹ | 9.70 |
| 10 | Trimethylol propane trimethacrylate | 3.89 |
| | Acrylic acid | 8.73 |
| | Cumene hydroperoxide | 1.89 |
| | Irgacure 184 ² | 3.00 |

Footnotes:

- 15 1 Acticryl CL1039 (which is a trade mark) is an acrylate ester supplied by SNPE or Harcros Chemicals Ltd; an equivalent of this product is Genomer M 200 (which is a trade mark) which is supplied by Rahn AG.
- 2 1-hydroxy-cyclohexyl-phenyl-ketone supplied by Ciba Geigy.
- 20 (Irgacure is a trade mark.)

The above composition was used to bond the end of an aluminium tube into a hole of corresponding diameter in an aluminium panel, by inserting the end of the tube, after degreasing, into the hole in the panel, applying the liquid sealant composition

25 around the join in sufficient quantity to penetrate the join by capillary attraction whilst leaving a continuous bead of uncured adhesive extending externally along the length of the join, and exposing the external bead of uncured adhesive to UV-radiation from a UV lamp. A strong, manually unbreakable bond was achieved in a matter of seconds. To develop the full strength of the adhesive bond, the assembly was heated

30 for 20 mins at 100°C. The join was shown to be completely water tight, even after immersion in 50:50 (vol) mixture of water and ethyleneglycol at boiling point for 48 hours.

The strong leak proof nature of the bond and its resistance to immersion in aqueous ethylene glycol (antifreeze) mixtures at boiling point, coupled to the rapid cure characteristics of the anaerobic sealant compositions demonstrates the clear utility of the composition in the manufacture of bonded radiator or heat exchange panels, e.g. radiators for use in the automobile industry, particularly as a strong leak proof bond can be obtained in a matter of seconds with only minimal preparation of the mating surfaces, i.e. it is generally sufficient merely to degrease the mating surfaces prior to bonding, with no need of any further treatment, for example, to remove oxide scale.

To measure the actual strength of the cured adhesive, the same adhesive was used to bond a 12.025mm diameter steel pin into a 12.05mm diameter hole (clearance 0.025 to 0.05mm) in a mild steel collar, both mating surfaces having a surface finish of from 0.4 to 0.5 μ m. The adhesive was injected between the mating surfaces leaving a fillet of uncured adhesive around the pin. This fillet was irradiated for 20 seconds with UV light from a UV lamp giving an intensity of 1814 μ W at 365nm, and then the assembled parts were heated at 100°C for 20 minutes to provide an accelerated and complete cure of the adhesive. After cooling to 23°C the joint strength was measured on a JJ tensometer Model TK30 at a jaw separation rate of 6mm.min.⁻¹. The maximum joint strength obtained in the several samples tested was 27.0MPa.

Each of these results is surprising.

Other modifications in the present invention described above and in the method of performing the invention will be apparent to those skilled in the art without departing from the scope of the invention herein described and hereinafter claimed.

CLAIMS

1. A curable coating composition comprising a curable monomer and at least one polymerisation initiator; wherein the curable monomer is a monoacrylate ester of the
5 formula (I)



10 where R is an alkyl or cycloalkyl group of up to 20 carbon atoms, or an alkyl or cycloalkyl group of up to 20 carbon atoms the carbon atom chain of which is interrupted by one or more ether oxygen atoms (-O-).

2. A composition according to claim 1 wherein the at least one polymerisation initiator is at least selected from: a radiation polymerisation initiator, an anaerobic
15 polymerisation initiator and a thermal polymerisation initiator.

3. A composition according to claim 2 wherein the at least one polymerisation initiator is at least a radiation polymerisation initiator and/or an anaerobic polymerisation initiator.
20

4. A composition according to claim 3 wherein the at least one polymerisation initiator is at least a radiation polymerisation initiator that is a photosensitive polymerisation initiator.

- 25 5. A composition according to claim 4 wherein the at least one polymerisation initiator is a UV polymerisation initiator.

6. A composition according to claim 1 wherein the composition is a UV-curable anaerobic adhesive coating composition comprising

- i) a monoacrylate ester of the formula (I) as defined in claim 1;
- ii) an anaerobic redox polymerisation initiator; and
- iii) a photosensitive initiator.

7. A composition according to any one of the preceding claims wherein the composition contains one or more other acrylate monomers selected from the corresponding esters of methacrylic acid, acrylic acid or methacrylic acid and the polyacrylic and methacrylic esters of acrylic or methacrylic acid and a polyfunctional alcohol or ether-alcohol.

8. A composition according to any one of the preceding claims wherein the composition contains up to about 60% by weight, based on the total composition, of a low molecular weight elastomeric polymer having a number average molecular weight in the range 1,000 to 6,000 and having one or more reactive groups in a pendant or terminal position on the elastomeric polymer molecule, such reactive groups being selected from: $-\text{CH}:\text{CH}_2$, $-\text{COOH}$, $-\text{SO}_2\text{Cl}$, $-\text{SH}$, $-\text{NH}_2$ and groups of the formula $-\text{OC}(\text{O})\text{C}(\text{R}):\text{CH}_2$ where R is H, $\text{C}_1\text{-C}_4$ alkyl or halogen.

9. A composition according to any one of the preceding claims wherein the monoacrylate ester is t.butylcyclohexyl acrylate.

10. A composition according to any one of the preceding claims wherein the composition contains a photoinitiator, and wherein the photoinitiator is of the free radical type.

11. A method of coating (all or partially) a first substrate, comprising coating the first substrate with a composition according to claim 1 or any claim dependent thereon, and exposing (all or part of) the coating to conditions to initiate polymerisation of the composition.

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12. A method according to claim 11 wherein the composition contains at least a UV polymerisation initiator and the method includes exposing (all or part of) the coating to UV radiation.

10 13. A method according to claim 11 wherein the composition contains at least an anaerobic polymerisation initiator and the method includes subjecting (all or part of) the coating to anaerobic conditions.

14. A method of forming an adhesive bond between a first substrate and a second
15 substrate, which comprises applying between the substrates a UV-curable anaerobic adhesive coating composition according to claim 6 or any claim dependent thereon, and exposing at least some of the applied adhesive coating to UV-radiation, thereby to initiate the photochemical cure of the adhesive, at least in the areas thereof that are exposed to the radiation, whilst allowing the remainder of the applied composition to
20 cure anaerobically.

15. A method according to claim 14, which comprises forming an adhesive join between a first substrate and a second substrate, which comprises applying the adhesive coating composition between the mating surfaces of the two substrates and
25 in a sufficient quantity to form an external bead of uncured adhesive along the line of the join, and exposing the external bead of uncured adhesive to UV-radiation thereby to initiate the photochemical cure of the bead, whilst allowing the adhesive between mating surfaces to cure anaerobically.

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16. A method according to claim 14 or claim 15 as applied to the formation of an adhesive bond between the end of a tubular first member inserted as a close fit in a correspondingly sized hole in a second member, and wherein said external bead of uncured adhesive completely encircles the said tubular member along the line of the
5 join between it and the said second member, thereby to form a fully leak-proof adhesive joint between the first and second members.
17. A method according to claim 16, as applied to the formation of a leak-proof adhesive joint between a tubular inlet of or an outlet connector to a heat exchange
10 panel as the first member and a heat exchange panel as the second member.
18. A method according to claim 17, wherein the heat exchange panel is a radiator for the cooling system of a motor vehicle.
- 15 19. A method according to any one of claims 11 to 18 wherein the first substrate is a metal substrate.
20. A method according to claim 19 wherein the first substrate is an aluminium substrate.
20
21. A method according to claim 11, as applied to the formation of an adhesive bond between two substrates, one of which at least is of glass, or other material transparent to UV-light, and wherein the photochemical cure of the applied adhesive is initiated by exposing the applied adhesive to UV-radiation through the UV-
25 transparent substrate.
22. A method according to claim 21, as applied to the formation of a glass-to-glass bond, a glass-to-metal bond or a glass-to-ceramic bond.
- 30 23. A solid coating comprising a cured coating composition according to claim 1 or any claim dependent thereon.

24. Use of a monoacrylate ester of the formula (I) as defined in claim 1 as a curable component of a coating composition.

25. Use of a monoacrylate ester of the formula (I) as defined in claim 1 as a UV-
5 curable component and/or an anaerobic curable component of a coating composition.

26. Use of a monoacrylate ester of the formula (I) as defined in claim 1 as both
a UV-curable component and an anaerobic curable component of a coating
composition.

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27. A UV-curable anaerobic adhesive coating composition substantially as
described herein and with reference to claim 1.

Relevant Technical Fields

- (i) UK Cl (Ed.N) C3P: PGD, PHL
 (ii) Int Cl (Ed.6) C08F 2/46, 2/48, 2/50

Search Examiner
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Date of completion of Search
 13 FEBRUARY 1995

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

Documents considered relevant following a search in respect of Claims :-
 1-27

(ii) ONLINE DATABASES: WPI, CLAIMS

Categories of documents

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| <p>X: Document indicating lack of novelty or of inventive step.</p> <p>Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.</p> <p>A: Document indicating technological background and/or state of the art.</p> | <p>P: Document published on or after the declared priority date but before the filing date of the present application.</p> <p>E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.</p> <p>&: Member of the same patent family; corresponding document.</p> |
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| Category | Identity of document and relevant passages | | Relevant to claim(s) |
|----------|--|--|----------------------|
| X | GB 2043659 A | (WESTINGHOUSE ELECTRIC) see Claims 1, 4, 5; Example 4 | 1-5 at least |
| X | GB 971938 | (W R GRACE) see Claim 1, all Examples | 1 at least |
| X | GB 861438 | (DUNLOP RUBBER CO) see Claims 1, 10; Table | 1 at least |
| X | GB 843854 | (KALLE & CO) see Claim 1, Example 11 | 1 at least |
| X | GB 741570 | (DU PONT) see Claim 1, Example V | 1-5 at least |
| A | EP 0328036 A1 | (HOECHST CELANESE) see Claims 1, 5; Examples | 1-5 at least |
| A | EP 0228565 A2 | (HENKEL) see Claims and Examples; page 2 lines 1-10; page 8 line 19 to page 9 line 4 | 1-6 at least |

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